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O₂ Adsorption on ZIF-8: Temperature Dependence of the Gate-Opening Transition

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Abstract

We present the results of an adsorption isotherm study of O₂ on the metal-organic framework ZIF-8. This material undergoes a structural transition (“gate-opening”) as a function of increasing pressure and sorbent loading which manifests itself in the isotherm data as a quasi-vertical substep. We used this feature to explore the temperature dependence of the structural transition; we have found that the transition occurs below the saturated vapor pressure only for temperatures below 93.93 K. The adsorption isotherm data measured at various temperatures was used also to determine the isosteric heat of adsorption of O₂ on this sorbent for different sorbent loading values. We have studied the adsorption kinetics for this system, i.e., how the equilibration times for adsorption change as a function of sorbent loading. The sorbent loading dependence of the equilibration time is non-monotonic; this characteristic appears to be related to the structural transition in the sorbent.

Keywords: MOF, Adsorption Kinetics, Isosteric Heat

1. Introduction

The discovery of porous metal-organic framework materials (a group of nanoporous materials consisting of metallic atoms linked by organic molecules that possess a crystallographically determined porous structure^{1,2,3,4,5}) has resulted in an explosive growth in the number of sorbents⁶ that are currently available both for study and for application.^{7,8} While most MOFs are produced in relatively small amounts (essentially for research purposes) there are a few individual MOFs that are produced in industrial quantities and are available commercially.⁹

Among the large number of MOFs that have been synthesized there is a group called ZIFs (for zeolitic imidazolate frameworks) that has topological structures similar to those of the zeolites. ZIFs are generally more thermally stable and more chemically robust than most other MOFs.¹⁰ This stability results from greater strength of the bonds between the organic linkers and the metal centers in these materials.¹¹

The ZIF that has most frequently been the object of study is ZIF-8. ZIF-8 is commercially available.⁹ Topologically, ZIF-8 has the sodalite structure; in ZIF-8 there are large pores interconnected by narrow windows.¹⁰ One of the features that makes ZIF-8 a particularly interesting MOF to study is that upon sorption ZIF-8 does not behave like an inert substrate, but rather like a flexible one¹² (a behavior not shared by zeolites). The sorption of a number of different gases on ZIF-8 can produce a structural transition in this material which also changes the sorption characteristics of this sorbent.^{12,13,14,15} The flexibility of ZIF-8 is reflected in the fact that atoms and molecules with kinetic diameters larger than that of the diameter of the “window” in the as-produced form of ZIF-8 can adsorb inside it (if the structure were rigid, such sorption would be sterically forbidden).¹²

The sorption-induced structural transition present in ZIF-8 belongs to a class of transitions called “gate-opening” transitions. These are transitions in which a relatively minor structural transformation results in an increase in the sorptive capacity of the material.¹⁶ For ZIF-8 this gate-opening transition corresponds to a sorption-induced re-orientation of the imidazolate linkers which otherwise leaves the structure (and the crystallographic group to which it belongs) unaltered.¹² The re-orientation results in an effective increase of the size of the interconnecting windows in the ZIF-8 structure and there is associated with it an increase in the amount of gas sorbed. In adsorption isotherm measurements the occurrence of this structural transition is

reflected by the appearance of an additional substep in the isotherms; the substep corresponds to sorption in the additional available space.^{11, 12, 13} The presence of the substep has been reported for adsorption measurements at cryogenic temperatures using various sorbates (Ar, CO, N₂ and O₂).¹³ The same structural transition was first identified as being present at room temperature in ZIF-8 when a pressure on the order of 1.4 GPa is applied to this material using a methanol-ethanol mixture as hydrostatic medium.¹⁷ Because of this room temperature result the low pressure structure of ZIF-8 is identified as ZIF-8AP (for As-Produced) while the phase present after the structural transition which exists at high-pressures is identified as ZIF-8 HP.¹²

This paper explores the temperature dependence of the gate-opening transition when molecular oxygen, O₂, is sorbed on a sample of ZIF-8 for temperatures in the range between 62.96 and 93.93 K. We have found that there is an upper temperature limit for which the gate-opening transition occurs at pressures below the saturated vapor pressure. The adsorption isotherm data measured at the various experimental temperatures were used to obtain the heat of adsorption for sorbent loadings below, at, and above the gate-opening transition. We have also investigated the adsorption kinetics of the O₂ as a function of loading on the ZIF-8. Specifically, we have determined the evolution of the adsorption equilibration time for gas sorption as a function of sorbent loading.

2. Experimental

The ZIF-8 used in these measurements was manufactured by BASF and purchased from Sigma-Aldrich as BASOLITE Z1200.⁹ The sample was placed inside a stainless steel cell sealed with a copper gasket. The sample was activated by heating it under vacuum to the recommended temperature of 170°C (starting from a temperature of 100°C in a process that took 24 hours). The sample was not re-exposed to air after activation. The mass of sample used was 0.1893 g. The O₂ gas used in the measurements was Research Grade O₂ from Airgas.

The adsorption measurements were conducted on a specially-built variable temperature adsorption setup that allows for the performance of adsorption measurements between 20 and 300 K.¹⁸ The long-term stability of the temperature control over a period of 24 hours was determined to be better than ± 50 mK over the entire range of temperatures explored, as was

determined from direct measurement of the saturated vapor pressures of O₂. The temperature of the stainless steel cell was controlled using a two temperature controller approach. One controller operating with a diode sensor set the temperature of the closed-cycle refrigerator cold-head providing rough control for the temperature of the sample cell (to within $\pm 0.5\text{K}$). The temperature of the sample cell was controlled using a separate temperature controller with a Pt sensor. The Pt sensor was calibrated during the experimental runs against the saturated vapor pressure values for O₂.¹⁹

The pressures were measured using three MKS capacitance manometers (they had, respectively, maximum pressure ranges of 1, 10 and 1000 Torr). The manometers sit at room temperature being part of the gas-dosing manifold. Standard thermo-molecular corrections (i.e., thermal transpiration corrections) were applied to all the measured pressure data.²⁰ These corrections are most important at pressures below 1 Torr and become more significant for the same pressure as the isotherm temperature decreases. The data were collected using an in-house developed program written in LabView.¹⁸

The kinetic measurements were performed by monitoring the evolution (decrease) of the pressure in the sample cell as a function of the time elapsed after each dose of gas was added to the stainless steel sample cell containing the ZIF-8 sorbent.²¹ The determination that equilibrium had been reached was made by inspection; equilibrium was deemed to have been reached when the pressure reached a fixed average value that was within the experimental noise of the measurements for a period of several hours.²¹ Because of the rather exacting equilibration conditions used in these measurements, completion of each adsorption isotherm took between a minimum of one and a half and a maximum of eight weeks with the majority of the isotherms taking longer than one month to complete. Details regarding the different portions of the setup and the measurements have been provided elsewhere.^{18, 21}

In addition to the full range of adsorption measurements, we have also conducted an adsorption-desorption isotherm. These measurements were made at liquid nitrogen temperature on an ASAP 2000 from Micromeritics with the purpose of comparing the results obtained with those available in the literature for the same sorbate.¹³ The sample of ZIF-8 used in these adsorption-desorption measurements was selected from the same batch of commercial ZIF-8 from which the sample that was used for all the other adsorption measurements was selected;⁹ its mass was 0.0897g.

3. Results

3.1 Adsorption measurements. We have measured seven full adsorption isotherms for O₂ on ZIF-8 spanning a temperature range between 62.96 K and 93.93 K. For reference the triple and critical temperatures for O₂ are, respectively, 54.361 K and 154.581 K.¹⁹ Consequently, all of the measurements reported here have been conducted above the triple point and below the critical point for molecular oxygen. Figure 1 displays a semi-logarithmic plot of all the isotherms measured in this study. The amount sorbed is given in mmols/gram and the pressure in Torr.

For all except the two highest temperatures measured the isotherms present two quasi-vertical substeps for pressures below the saturated vapor pressure (the saturated vapor pressure is marked in the sorption data by the vertical step present at the highest pressures for each temperature).

The lower pressure quasi-vertical substep, that spans a greater sorbent loading interval, corresponds mostly to the sorption of O₂ on the as-produced form of the sorbent ZIF-8AP.¹² This region is followed by a small slope region in which pressure increases rapidly with little increase in sorbate loading. The small slope region ends at the foot of the second quasi-vertical substep in the isotherm. This higher pressure substep corresponds to gate-opening and to the adsorption of O₂ on the additional sorptive volume that becomes available as a result of the structural transition.¹² Soon after the high pressure substep is completed all the pore space available in the ZIF-8 sorbent is filled with O₂ and further doses of gas quickly reach saturation; additional doses added to the sample cell just fill the volume of the cell with liquid O₂ at the fixed value of the pressure corresponding to saturation for that temperature.

Inspection of the data presented in Figure 1 shows (without the need for doing any calculations) that as the isotherm temperatures are increased the value of the pressure at which the second step appears increases and approaches the value of the saturated vapor pressure. As the isotherm temperatures are increased, eventually the higher pressure step feature disappears. Consequently, the lack of a substep on a sub-critical adsorption isotherm performed on ZIF-8 is not necessarily an indication that the gate-opening transition does not take place for a given system; rather, it is more likely an indication that the temperature at which the measurements were conducted were not sufficiently low to find evidence of this feature below saturation.

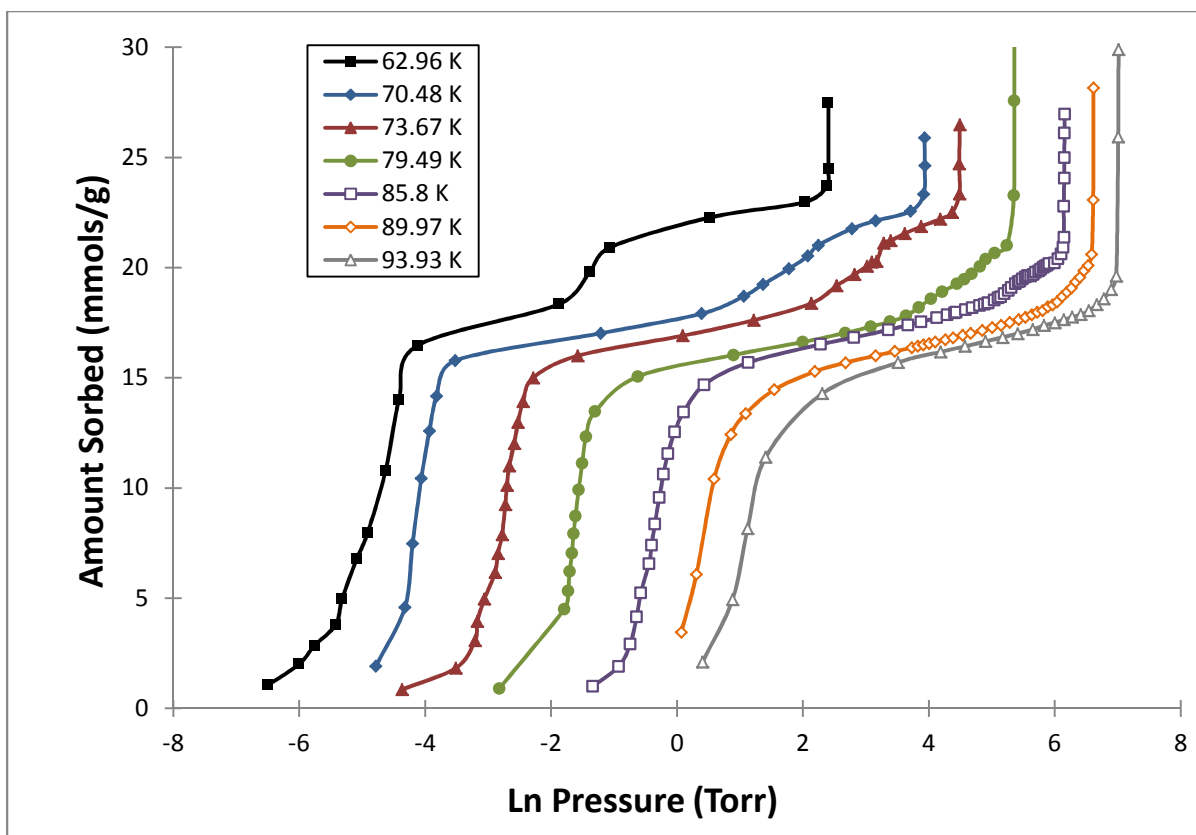


Figure 1. Adsorption isotherms of O₂ adsorbed on the metal-organic framework ZIF-8 at seven different temperatures between 62.96 K and 93.93 K. Vertical lines at the highest loadings correspond to the pressure reaching the saturated vapor pressure for the corresponding temperature. The smaller substep present between loadings of 15 and 21 mmols/g corresponds to the gate-opening transition in ZIF-8.

In order to compare directly our results with those previously reported in the literature for O₂ on this same sorbent we have also performed a set of adsorption-desorption measurements.¹³ These are displayed in Figure 2. The results displayed are in very good agreement with those that are reported in reference 8 (the data corresponding to O₂ is presented in the lower left of Figure 3 in Reference 8). The adsorption-desorption data displayed in Figure 2 were measured on a Micromeritics ASAP 2020 automatic adsorption isotherm apparatus with the sample in a liquid nitrogen bath.

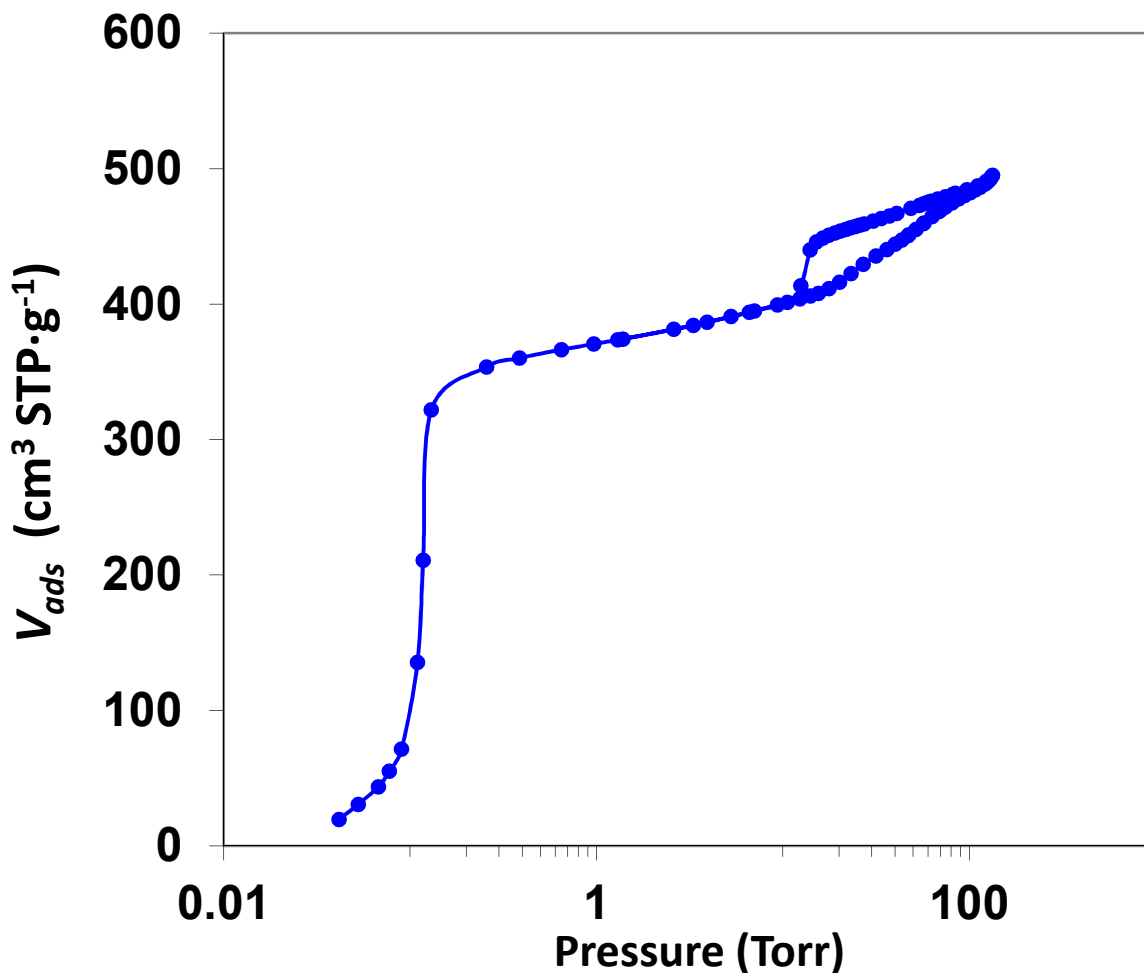


Figure 2. O_2 adsorption-desorption isotherm on ZIF-8. These data were measured at liquid nitrogen temperature on a Micromeritics ASAP 2020 apparatus.

We can obtain an estimate of the *effective* specific surface area corresponding the sorption in our ZIF-8 samples using the point B method.²² Figure 3 shows a linear plot of the adsorption isotherm corresponding to the lowest measured temperature, 62.93 K. Application of the “point B” method yields an *effective* monolayer capacity of 22.24 mmols/g. Note that because sorption is occurring in pores the “point B” does not correspond to the monolayer capacity; the *effective*

monolayer is the capacity that an O₂ monolayer would have if the same number of oxygen molecules were adsorbed on a flat surface rather than on a porous sorbent. Assuming that the specific surface area for adsorption of O₂ on a flat surface is 12.5 Å²/molecule (that is, the surface density corresponding to the δ phase of molecular oxygen on exfoliated graphite in which the long molecular axis is parallel to the surface of graphite),²³ we obtain a value of the effective surface area for our sample of 1,675 m²/g. This estimate is somewhat uncertain, because if one assumes a denser packing for O₂, for example that corresponding to the ζ phase²³ of O₂ on graphite (which has a specific area of 9.09 Å²/molecule), the estimate for the effective specific surface area becomes 1,218 m²/g.

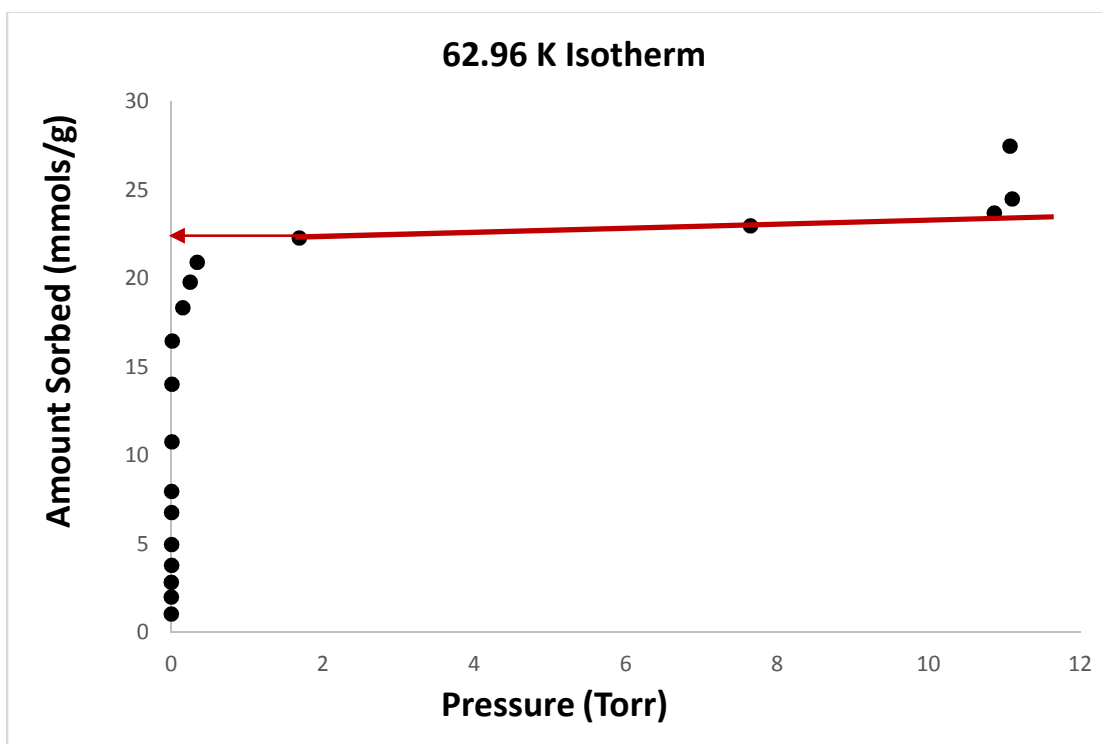


Figure 3. Linear plot of the adsorption isotherm at 62.96 K for O₂ on ZIF-8. The determination of the effective monolayer capacity of the MOF sample is done using the Point-B method.²² The “effective monolayer” includes the region corresponding to adsorption after the gate-opening transition.

We note that the linear extrapolation shown in Figure 3 is carried out at pressures above that of the gate-opening pressure for this temperature. The effective specific area obtained is in good agreement with reported values for this quantity.^{10,13,24}

The specific pore volume for the sample can also be obtained from the adsorption isotherm data by measuring the total amount of molecules adsorbed on the sorbent just before the saturated vapor pressure is reached (which is done from a linear extrapolation of the amount adsorbed to saturation, also using the data of Figure 3). The number of molecules is then multiplied by the volume per molecule for the sorbate in its liquid phase at the isotherm temperature¹⁹ to obtain the estimate for the pore volume in the sorbent. This yields a pore volume of 0.598 cc/g.

4. Heats of Adsorption and Transformation

The isosteric heat of adsorption is the amount of energy that is released when an atom or molecule of the sorbate is adsorbed under constant sorbent loading conditions.²⁵ In the limit of low sorbent loading and low temperatures this quantity is directly related to the binding energy of the sorbate on the strongest binding sites on the sorbent.

The isosteric heat of adsorption, q_{st} , can be measured directly calorimetrically; however, most often it is determined from adsorption isotherm data measured at several different temperatures. Equation (1) provides the connection between the isosteric heat, q_{st} , and the isotherm data:²⁵

$$q_{st} = kT^2 \left(\partial \ln P / \partial T \right)_n \quad (1)$$

here k is Boltzmann's constant, T the isotherm temperature, n is the constant value of the sorbate loading, and P is the value of the pressure for loading n and temperature T .

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3 A plot in which the logarithm of the values of the pressure at a fixed sorbent loading as a
4 function of the inverse of the isotherm temperature yields a straight line. The slope of the line is
5 directly proportional to the isosteric heat of adsorption for that value of the sorbent loading.
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9 In Figure 4 we present such plots for three different values of the surface loading: the lowest
10 line is determined from values taken at the middle of the low-pressure substep that corresponds
11 to adsorption on ZIF-8 AP (for $n = 12.41$ mmols/g); the middle line corresponds to a loading in
12 the region of the higher pressure substep (adsorption of O_2 on the ZIF-8HP; the data is taken for
13 $n = 18.64$ mmols/g) and the top line curve corresponding to the saturated vapor pressure for
14 molecular oxygen.
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19 The procedure described above for the case of the saturated vapor pressure yields the
20 Clausius-Clapeyron equation applied to the data when the gas is approximated as ideal. Solving
21 the resulting Equation (1) we obtain:
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$$\ln(P_{sat}) = \frac{-A}{T} + B \quad (2)$$

24 where $A = L_{transition}$, is the latent heat corresponding to the transition (in this case is the value of
25 the latent heat of vaporization).
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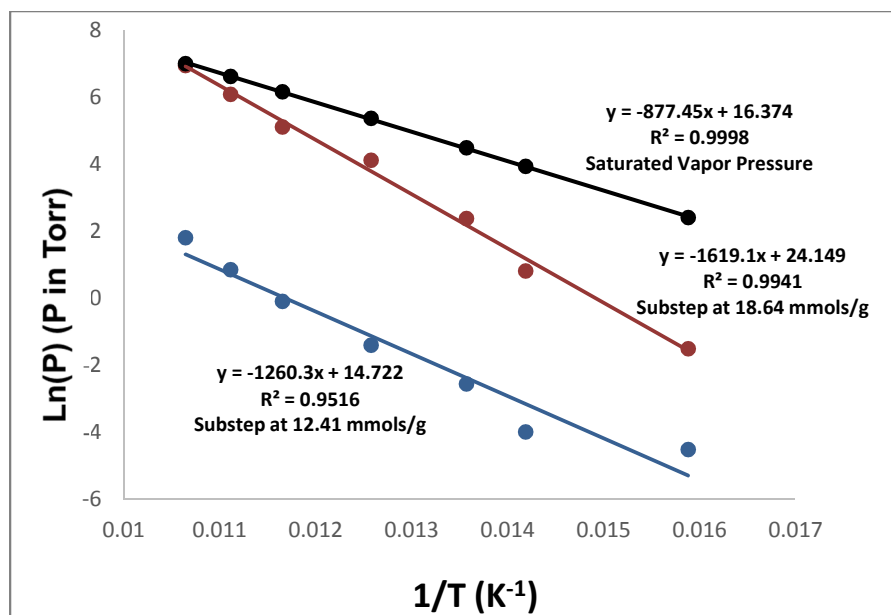


Figure 4. Plot of $\ln(P)$ vs $1/T$ for three different sorbent loadings from the isotherms of O_2 adsorbed on ZIF-8 at temperatures between 62.96 K and 93.93 K. The points along the steepest line correspond to pressures measured on the higher loading substep for the different isotherm temperatures; these data were measured at a loading of $n = 18.64$ mmols/g. The line with slope -877.45 displays the saturated vapor pressure for oxygen. The line with slope -1260.3 corresponds to data measured on the lowest pressure substep (the value of the constant loading used to determine this line was $n = 12.41$ mmols/g).

We look first at the line corresponding to the saturated vapor pressure. The slope of this line yields a value for the latent heat of vaporization of 75.6 meV per molecule. This compares quite favorably with the reported value of the latent heat of vaporization of O_2 , of 70.7 meV (the agreement is to within 7 % of the reported value).²⁶

Using the same approach for the data corresponding to the heat of adsorption for the sorption of O_2 on the ZIF-8AP (i.e., from the data corresponding middle of the lower-pressure isotherm substep) we obtain that this quantity is $q_{st} = 104$ meV per molecule.

Finally, for the heat evolved for the process corresponding to the higher-pressure substep in the isotherm data we obtain a value of 136 meV. This heat evolved corresponds to the processes

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3 taking place upon adsorption on these sites. We can assume that these can be separated into two
4 parts: one corresponding to the heat of adsorption on the resulting sites available for adsorption,
5 and another part corresponding to the heat evolved in the structural transition on the ZIF-8.²⁷
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9 We can get an idea of the magnitude of the latter by making the assumption that the portion
10 of the heat evolved corresponding to the heat of adsorption of O₂ on the ZIF-8 will be equal to
11 what it is in the ZIF-8AP. (This is not strictly a correct assumption as the sorption sites are
12 different, but it is useful to give an estimate for the order magnitude of the heat of transformation
13 involved in the structural transition). Making this assumption, we obtain an estimate for the heat
14 of transformation of about 30 meV, or roughly one fourth of the total heat evolved measured for
15 this process.
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21 Extrapolating the line representing the sorption data on the high-pressure substep in Figure 4
22 (middle line) we see that it intersects the line corresponding to the O₂ saturated vapor pressure at
23 a temperature of 95.39 K. What this means is that in O₂ adsorption isotherms measured at
24 temperatures between 95.39 K and the critical temperature for O₂, the saturated vapor pressure
25 will be reached *before* the higher pressure substep is reached. Since adsorption isotherms
26 measured below the critical temperature stop once the pressure reaches saturation, what we will
27 have is that for isotherms measured at those temperatures there will not be two substeps in the
28 adsorption data; only the lower pressure substep will be present. That this is, in fact, the case is
29 strongly suggested already by the data corresponding to the highest measured isotherm, at T =
30 93.93 K. There is no longer a substep at high pressures in this isotherm, although there is a
31 modest increase in the amount sorbed as saturation is approached which is higher than that seen
32 in the vicinity of saturation at lower temperatures. Unfortunately, limitations in the pressure
33 ranges of the gauges available in our setup prevented us from extending our adsorption
34 measurements beyond this temperature.
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46 An intriguing possibility is suggested by the data of Figure 4. If the lines corresponding to
47 the lower pressure substep and the higher pressure substep are extended to low temperatures, we
48 expect that they will intercept for $(1/T) = 0.02556$ or $T = 39.1$ K. The likely scenario for this case
49 is that since gate-opening will happen below the pressure at which most of the adsorption takes
50 place in the ZIF-8, there will be only one step present at temperatures below this point.
51 Unfortunately in this case the expected value of the crossing pressure (approximately 3.2×10^{-8}
52 Torr) is much too low to be measurable with the capacitance gauges in our adsorption setup.
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5. Kinetics of Sorption

Figure 5 shows fractional pressure change relative to the equilibrium value of the pressure P_{eq} , $[P(t)-P_{eq}]/P_{eq}$, as a function of the time elapsed since the gas dose was added to the sample cell, for approximately one half of the data points along the sorption isotherm measured at 70.48 K. In these curves, equilibrium corresponds to a line parallel to the horizontal axis. (The curves shown in Figure 5 have been displaced vertically by arbitrary amounts for the sake of clarity.) Not all curves are shown from their initial times (i.e., $t = 0$). This is done in order to show in Figure 5 the relevant portion of the data, i.e., where equilibrium is reached, in sufficient detail and clarity.

The point number is the number along the isotherm, starting from the lowest loading (i.e., higher point numbers correspond to greater sorbent loading). The lowest three points shown (points 1 and 5) have equilibration times on the order of 10^5 seconds (approximately 28 hours). These points are along the lower pressure substep section of the isotherm. There is a slight decrease in the time required to reach equilibrium as the sorbent loading increases for these points. The equilibration time decreases for point 8 (in the small-slope region of the isotherm, above the lower pressure substep), and the equilibration time decreases even more sharply as the loading increases in this region (point 10). Beyond point 13, the equilibration times increase again (for points 13, 14 and 15). These points correspond to the higher pressure substep. Once the loading corresponding to this substep is completed, the equilibration time decreases quickly to its lowest value (point 17 and 18).

It is important to note that the equilibration times listed here for individual data points along the isotherm are in general much longer than most of those reported in the literature for adsorption on MOFs. Many of the reported adsorption isotherm measurements are performed with the sample cell immersed in a bath of cryogenic liquid. Hence, for them the measurement times are ultimately dictated by how long the cryogenic bath lasts. This is not the case in our setup. Using a closed cycle refrigerator to achieve the low temperatures we can determine equilibration to a more exacting standard.

The observed non-monotonic behavior of the equilibration times as a function of sorbent loading was unexpected. This behavior is different from that observed for adsorption on surfaces, where, depending on the characteristics of the sorbate, the equilibration times either monotonically increase or monotonically decrease with loading. The non-monotonic behavior occurs in the region of the isotherm that corresponds to the gate-opening transition, so the non-monotonicity appears to be related to the presence of the structural transition on ZIF-8.

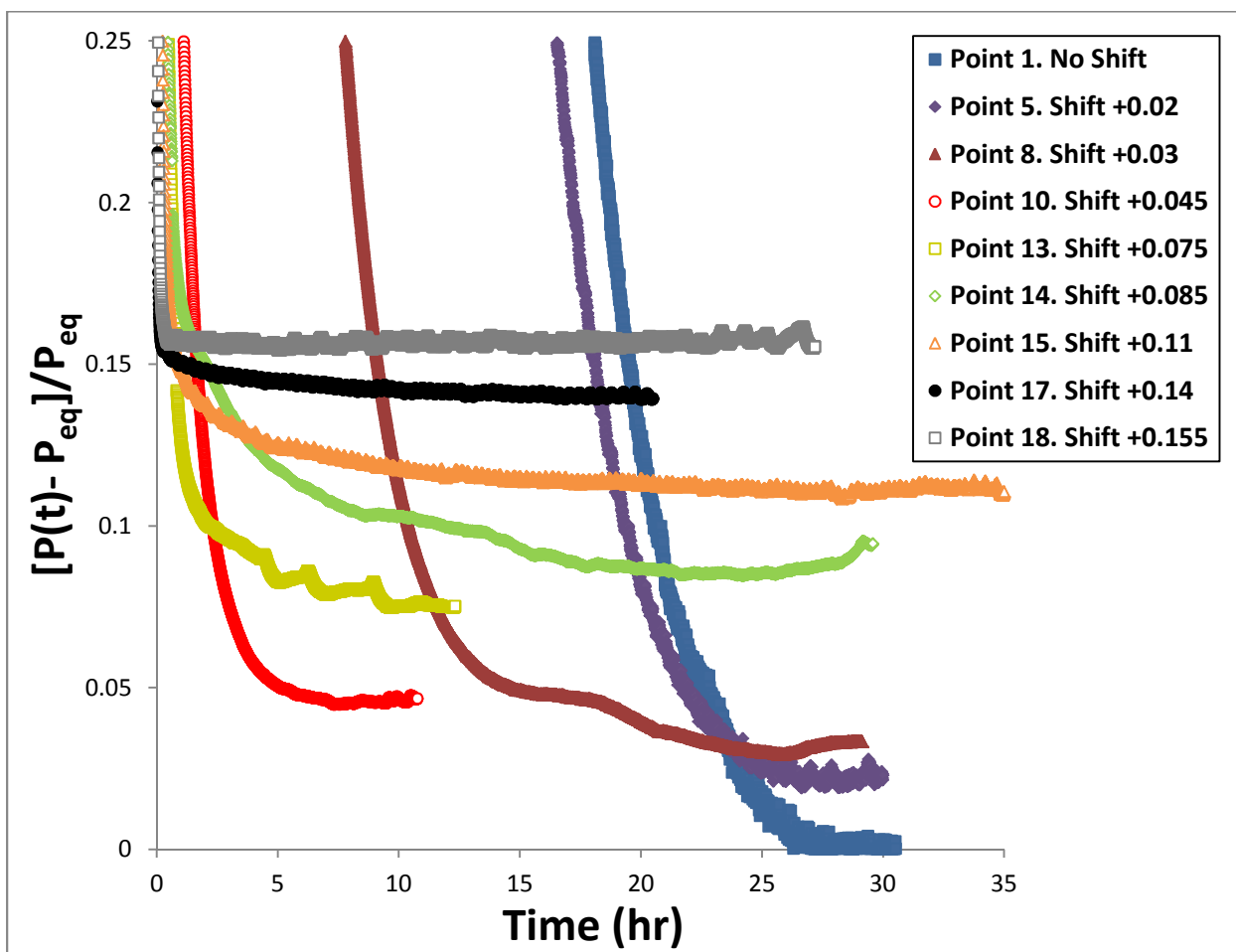


Figure 5. Fractional Pressure vs. time plots for selected points along the 70.48 K isotherm. The point numbers indicate the point along the isotherm sequence in which a data were measured (e.g., point 1 is the first point along the isotherm, the one measured for the lowest loading, etc. etc.). The evolution of the equilibration time is a non-monotonic function of the sorbent loading. For low loadings (see points 1, 5 and 8) the equilibration times are quite long. As the loading increases to the small-slope portion of the isotherm (rapid increase in pressure for small increases

in loading) the equilibration times become short (see point 10). In the region corresponding to the structural transition substep the equilibration times increase again (points 13, 14 and 15). And for loadings beyond the substep (points 17 and 18) the times become very short.

6. Conclusions

We have explored the temperature dependence of the gate-opening transition for O₂ on ZIF-8 in the range between 62.93 and 93.93 K. Over most of these temperatures the gate-opening transition results in the presence of a second, higher-pressure quasi-vertical substep in the adsorption data. This substep appears increasingly closer to saturation as the temperature of the isotherms increases. From plots analogous to the Clausius-Clapeyron equation we estimate that the substep corresponding to the gate-opening transition will occur at pressures higher than the saturated vapor pressure for temperatures above 95.39 K. That is, subcritical isotherms measured up to saturation for temperatures above 95.39 K will not show evidence of a gate-opening transition substep.

We have calculated the isosteric heats, q_{st} from the adsorption isotherm data and we find that for the adsorption of the as-produced form of ZIF-8 (ZIF-8AP) the isosteric heat of adsorption for O₂ is 104 meV per molecule. This value remains substantially constant for the entire range of coverages in this region. The isosteric heat involved in the gate-opening transition and in the adsorption of O₂ on the additional sorption sites that become available as a result is 136 meV per molecule. If we make the assumption that the isosteric associated with the adsorption on the additional sites that become available is the same as the isosteric heat on the ZIF-8AP, we obtain an estimate of approximately 30 meV for the heat evolved in the structural gate-opening transition.

Our results for the adsorption kinetics of this system indicate that reaching equilibrium requires relatively long equilibration times (between two and more than twenty five hours per

data point). We note that these values are considerably longer than those reported on much of the literature on MOFs. The equilibration times on the ZIF-8AP sites are a decreasing function of sorbent loading (and, more importantly, perhaps, of the equilibrium pressure). However, the evolution of the equilibration times is non-monotonic. Equilibration times increase with loading in the gate-opening region of the isotherm, and, once this region is completed, these times decrease again as the equilibrium pressure approaches saturation and the sorbent loading increases. The explanation for what occurs at gate-opening is not clear, at this point. The rest of the behavior is what one would expect for a system of fully accessible, open pores at their two ends that is not diffusion limited: as the pressure increases, so do the gas collisions with the sorbent, and the chances of adsorption; consequently, the equilibration times decrease.

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Supporting Information

Figure 6 displays mass loading as a function of time for select points from the 70.48 K isotherm using the linear driving force model. Also given in Figure 7 are the equilibration times as a function of sorbent loading for that same isotherm. This information is available free of charge via the internet at <http://pubs.acs.org>.

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